

PATENT SPECIFICATION

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(54) METHOD OF PRODUCING TIN-PLATED STEEL SHEET

(71) We, KAWASAKI STEEL CORPORATION of No.1—28, 1-Chome, Kitahonmachi-Dori, Fukiai-Ku, Kobe City, Japan, a company organized according to the laws of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing tin-plated steel sheet, and more particularly but not exclusively to a method of producing a corrosion resistant tin-plated steel sheet for use in manufacturing cans for containing acidic foods.

In general, a tin-plated steel sheet consists of a steel sheet, an alloy of the iron and tin, a tin layer, a passivation film and an oil coating. The function of each of these layers is well known in the art.

The covering ratio of the iron-tin alloy layer is the most essential element for determining the corrosion resistance of tin-plated steel sheet. If the tin-plated steel sheet is used to manufacture cans for, for example, acid fruit juice, it is important that the steel sheet shall be compactly and uniformly covered with the iron-tin alloy layer in order to restrict the dissolution rate of tin, whereby the tin-plate can is given a longer shelf life.

In order to produce a highly corrosion resistant tin-plated steel sheet, a number of methods of modifying the iron-tin alloy layer have been proposed. These methods, however, are not always effective enough to improve the corrosion resistance of the tin-plated steel sheet or are not always easy to carry out in practice. In addition, conventional methods in which the corrosion resistance of the tin plate is based on the iron-tin alloy layer are not able to produce sufficiently high corrosion resistance in killed steel.

According to the present invention there is provided a method of producing tin-plated steel sheet which comprises

- (i) treating a steel sheet with nickel, copper or a nickel-tin alloy to form a coat-

ing thereon having a thickness of from 0.005 μ to 0.05 μ ;

- (ii) heating the coated steel sheet in a non-oxidising atmosphere to completely diffuse the nickel, copper or nickel-tin alloy into the steel to form a reformed steel sheet; and

- (iii) plating the reformed steel with tin to form the desired tin-plated steel sheet.

The steel sheet to be treated and tin-plated according to the invention may be for example rimmed steel sheet or killed steel sheet.

The step of heating the coated sheet may be carried out by, for example, a continuous annealing operation or a box type annealing operation.

It is possible to produce matte finish tin-plated steel sheet having increased corrosion resistance. However, in a preferred embodiment the tin-plated steel sheet produced by the method of the invention is subjected to a reflow treatment.

It is believed that complete penetration and diffusion of the coating metal or alloy into the steel sheet produces a reformed steel sheet surface wherein corrosion producing galvanic current caused by electrical contact between the steel sheet surface and the tin layer in, for example, acidic fruit juice, is decreased. In a tin-plated steel sheet produced in accordance with the invention no iron-tin alloy layer seems to be present at the interface between the finally plated tin layer and the reformed steel sheet. The steel sheet surface, however, is electrochemically reformed, and as a result, the electrode potential produced at the steel sheet is almost the same as that produced at the tin layer so that negligibly small galvanic current flows even when the steel sheet is short circuited to the tin layer.

In one embodiment of the invention, a steel sheet is cold rolled to reduce it to a desired thickness, electrolytically cleaned, washed with water, slightly pickled and then again washed with water. The steel sheet thus cleaned is introduced into a plating cell to plate a metal coating having a given thickness and consist-

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ing of nickel, copper or nickel-tin alloy directly upon the clean steel sheet. In this case, it is important that the steel sheet be compactly and uniformly covered with the coating of metal or alloy.

For carrying out the coating operation, an electroplating operation may preferably be effected. A substitution plating may also be effected with nickel, copper or a nickel-tin alloy which is capable of effecting such substitution plating.

The coated steel sheet is washed with water, dried, immediately thereafter reeled, and then is heated in a non-oxidising atmosphere to a temperature which is sufficient to alloy the coating metal or alloy with steel sheet. It has been found that the penetration and diffusion of the coating into the steel, due to the heat treatment, may be attained by a continuous annealing operation or by a box type annealing operation which is commonly applied to steel sheet after it has been cold rolled.

The annealing time may be determined in dependence on the thickness of the coating and the annealing temperature such that the coating of metal or alloy penetrates and diffuses into the metal sheet to such an extent that a reformed steel sheet surface, where the coating substantially disappears, is obtained.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:

Figure 1 graphically illustrates the relationship between the heating time required for complete disappearance of a nickel layer from the surface of a steel sheet by penetration and diffusion of the nickel into the steel so as to obtain a reformed steel sheet surface, the thickness of the nickel layer and the heating temperature;

Figure 2 graphically illustrates the relationship between the ATC value obtained by an ATC test carried out on a tin-plated and reflowed steel sheet treated with nickel by the method of the invention, the heating time at a heating temperature of 700°C, and the initial thickness of the nickel coating layer. This figure also includes results obtained from an untreated steel sheet;

Figure 3A shows schematically a section of a tin-plated reformed steel sheet produced by the method of the invention and having a pin-hole in the tin-plated layer;

Figure 3B shows schematically a section of a reflowed, tin-plated steel sheet obtained following the method of the invention but with incomplete diffusion of the coating metal or alloy into the steel;

Figure 3C shows schematically a section of a tin-iron alloy layer formed between a plated tin layer and a steel sheet obtained by a conventional method;

Figure 4A shows a microscopic photograph

of the tin-plated reformed steel sheet of Figure 3A with 10,000 times magnification; and

Figure 4B shows a microscopic photograph of the conventional tin-iron alloy layer of Figure 3C with 10,000 times magnification.

Referring to Figure 1, it was found that depending upon the initial coating thickness and upon the method of heating, the time for the complete disappearance of the coating was from about a minute to several hours. Heating by a continuous annealing operation took from 1 minute to 10 minutes at from 600 to 800°C, while heating by a box annealing operation took from 30 minutes to 10 hours at from 600 to 800°C.

Whether or not the plated metal or alloy layer remains on the steel sheet surface may be determined by peening, with the aid of a dilute acid, the layer which remains at the surface of the steel sheet after it has been heated to effect penetration and diffusion into the steel, and by subjecting the layer thus removed to an electron diffraction analysis.

Referring to Figure 2, the ATC value (Alloy-tin couple value) shows the corrosion current flowing between a pure tin electrode and an iron-tin alloy electrode, the ATC value being measured in units of μA (microamperes)/ cm^2 .

The measurement is made after 20 hours exposure of the electrodes in a medium consisting essentially of deaerated grapefruit juice. The higher the corrosion resistance of tinplate the lower the ATC value.

As may be seen from Figure 2, the ATC values of the nickel plated steel sheets are far superior to that of a steel sheet not plated with nickel. In addition, the ATC values of the nickel plated steel sheets rapidly improve (minimise) as the heating time increases and reach a minimum value at a certain heating time, further increase in heating time resulting in a gradual increase of the ATC values.

It has been found that the time at which the ATC value reaches a minimum is equal to the time at which complete disappearance of the plated metal or alloy just occurs. Advantageously, therefore, heating at 600 to 800°C is effected for a time just sufficient for this to happen.

In accordance with the invention the initial coating of nickel, copper or nickel-tin alloy must be limited in thickness to from 0.005 μ to 0.5 μ . This is because of the fact that if the initial metal or alloy coating thickness is less than the lower limit, 0.005 μ , such a thin metal coating does not contribute to corrosion resistance in the finished plated sheet. If the initial metal or alloy coating is thicker than the upper limit, 0.5 μ , the heating operation must be effected for a relatively long time and is thus not economical and hence not applicable in practice. In addition, the use of an initial metal or alloy coating thicker than 0.5 μ gives the disadvantage that non-diffused coating metal or alloy remains on the steel sheet sur-

face even after the heating operation has been completed, thereby degrading the ATC value and producing further disadvantages which will be described hereinafter.

Whether or not the metal or alloy coating remains on the steel sheet surface after it has been heat treated can easily be confirmed by such techniques as electrolysis or X-ray diffraction.

Tests have shown that if the metal or alloy coating remains on the steel sheet surface after heating to promote penetration and diffusion thereof, the following disadvantages may occur.

(1) Tin-plated metal sheet not subjected to a reflowing operation.

If the coating of metal or alloy completely penetrates and diffuses into the steel sheet surface to produce a reformed steel sheet surface, the electrode potential of the steel sheet surface in an organic acid such as grapefruit juice being almost equal to or slightly lower than the electrode potential of tin. As a result, even when the tin is short circuited to the reformed steel sheet surface, substantially no galvanic current flows between the tin electrode and the steel sheet electrode, whereby the dissolution rate of tin is very small.

On the contrary, if the coating of metal or alloy remains on the steel sheet surface, the electrode potential of the steel sheet surface in the above mentioned organic acid becomes more negative with respect to that of the tin. As a result, if the tin is short circuited to the steel sheet surface, a rapid dissolution of the coating of metal or alloy through pinholes or deteriorated portions of the tin layer into the organic acid occurs, thereby degrading the organic acid.

(2) Tin-plated steel sheet subjected to a reflowing operation.

A tin-plated steel sheet obtained from a steel sheet into the surface of which a coating of metal or alloy has been completely penetrated and diffused, forms a compact alloy layer at the interface between the coated tin layer and the reformed surface during a reflowing operation.

Referring to Figure 3A there is shown a section of reformed steel sheet surface comprising a compact alloy layer 1 formed during reflowing, a plated tin layer 2, a reformed steel sheet surface 3 and a steel sheet 4.

Figure 4A shows a photograph of the compact alloy layer 1 of Figure 3A taken by an electron microscope having a magnification of 10,000.

As may be seen from Figures 3A and 4A the reformed steel sheet 4 is covered with the compact alloy layer 1 which consists of extraordinarily fine crystals. Even when the steel sheet 4 is exposed through pinholes eventually formed in the tin layers 2, the presence of the reformed steel sheet surface 3 and compact alloy layer 1 is capable of markedly decreasing the dissolution rate of the tin. Thus, the tin-

plated steel sheet produced by the method according to the invention and as shown in Figures 3A and 4A has improved its corrosion resistance by virtue of the synergistic effect of the reformed steel sheet surface 3 and the compact alloy layer 1.

Referring to Figure 3B there is shown a section of the tin plate which is obtained after reflowing by using a steel sheet where the coating of metal or alloy remains on the steel sheet surface after the steel sheet has been subjected to the heating operation. In this case, the alloy layer formed has a loose structure and is black in colour. This alloy layer 1 can be distinguished from the compact alloy layer 1 shown in Figure 3A and can easily be rubbed off.

If tin is dissolved out of the inner surface of the can into food products to expose the alloy layer, it is desirable that the alloy layer thus exposed is attractive in colour, and that contact between the exposed alloy layer and the contents of the can does not result in the contents being deteriorated in appearance by contamination.

Such a loose alloy layer does not contribute to the improvement in the corrosion resistance of the tin-plated steel sheet, and in addition, the surface tin of the tin-plated steel sheet is consumed by the formation of the alloy so as to reduce the free tin which can protect the steel sheet from corrosive substances. Moreover, the coating of metal remaining on the steel sheet surface results in a reduction of the tin crystal size of the tin-plated steel sheet after the reflowing operation, which in turn results in a deterioration in the corrosion resistance of the tin-plated steel sheet.

Figure 3C shows a section of a tin-iron alloy layer 1 of a conventionally tin-plated rimmed steel sheet. Figure 4B shows a photograph of that tin-iron alloy layer 1, taken by an electron microscope.

In the prior art technique by which nickel or other metal is coated upon the steel sheet immediately before the tin-plating operation is effected, an alloy layer is formed when the tin is subjected to the reflowing operation which is of an undesirable loose form, black in colour and easily rubbed off. In addition, the metal plated upon the steel sheet immediately before the tin-plating operation, when heated at a temperature which melts the tin only, is rapidly diffused into the melted tin, and as a result, substantially no diffusion of the coated metal into the steel sheet occurs. Thus, the property of the steel sheet *per se* is not reformed at all.

The following Examples illustrate the invention.

Example 1.

A rimmed steel sheet was cold rolled, electrolytically cleaned, washed with water, slightly pickled, and then washed with water. The rimmed steel sheet thus treated was plated

in a standard plating bath with a nickel coating 0.1 μ thick. This nickel plated steel sheet was washed with water, dried and then subjected to a box type annealing operation at a temperature of about 650°C for six hours, whereby the plating metal completely penetrated and diffused into the steel sheet to provide a reformed steel sheet surface. A rimmed steel sheet treated as described above but without being subjected to the nickel plating operation was directly subjected to the above described box type annealing operation for the sake of comparison.

The above two rimmed steel sheets, respectively plated with and not plated with the

nickel coating, were electrolytically cleaned, washed with water, slightly pickled and then electroplated with a tin coating 5.6 g/m² thick (one side) in a halide bath.

The two tin-plated steel sheets were washed with water, dried, subjected to an electric resistance heating operation to heat and melt the tin coating and then subjected to a cathodic chemical treatment in sodium dichromate to provide two finished tin-plated steel sheets. An ATC test (alloy-tin couple test), a hot water test and an Iron Solution Test were effected on the tin-plated steel sheets, and the results obtained are shown in Table 1.

TABLE 1

Kind of Sample	Test Results			
	ATC Value (μ A. ² /cm ²)	ISV* (μ g./cm ²)	Number of pinholes per 1 cm ²	Tin** Crystal Size
Tin-plated steel sheet treated by the method according to the invention	0.050	0.06	0 to 10	\approx 8
Tin-plated steel sheet for comparison	0.150	0.35	30 to 50	\approx 8

* ISV (iron solution value) is the amount of iron dissolved (expressed as μ g (micrograms)/cm²) when the ISV test for measuring certain characteristics of electrolytic tin plate which affect internal corrosion resistance is carried out. The ISV test involves the colorimetric determination of the total amount of iron dissolved when 3.14 in² of tin plate surface are exposed for 2 h. at 80 \pm 1°F to 50 ml of a mixture of dilute sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), and ammonium thiocyanate (NH₄SCN).

** If the surface of a tin-plated steel sheet is slightly etched by acid or alkaline solution, it is possible to detect a tin crystal size with the aid of a microscopic photograph. Grain size standards for tin plate coatings, for example \approx 8 are defined in W. E. Hoare, E. S. Hedges and R. T. K. Barry, "The Technology of Tin Plate", (1975), page 285 (Edward Arnold Limited, London).

As may be seen from Table 1, treatment by the method according to the invention can considerably improve the corrosion resistance of the rimmed steel sheet.

Example 2.

A continuous moulded aluminium-silicon

killed steel sheet was cold rolled and then treated in the same manner as in Example 1 to obtain two tin-plated steel sheets corresponding to those obtained in Example 1, which were then subjected to the same tests as those described in that Example.

TABLE 2

Kind of Sample	Test Results			
	ATC Value ($\mu\text{A}/\text{cm}^2$)	ISV ($\mu\text{g}/\text{cm}^2$)	Number of pinholes per 1 cm^2	Tin Crystal Size
Tin-plated steel sheet treated by the method according to the invention	0.40	0.06	0 to 10	# 8
Tin-plated steel sheet for comparison	0.175	0.45	30 to 50	# 8

As may be seen from Table 2, the method according to the invention can significantly improve the corrosion resistance of the continuous moulded aluminium-silicon killed steel sheet.

Example 3.

A rimmed steel sheet was cold rolled, electrolytically cleaned, washed with water, slightly pickled, and then washed with water.

The rimmed steel sheet thus treated was plated in a standard plating bath with a $0.5\text{ }\mu$ thick nickel coating. This nickel plated steel sheet and another steel sheet not plated with nickel were washed with water, dried and then subjected to a box type annealing operation at a temperature of 700°C for 6 hours, whereby

the plating metal was completely penetrated and diffused into the steel sheet.

The rimmed steel sheets treated as above were further electrolytically cleaned, washed with water, slightly pickled, again washed with water and then electroplated with a tin coating $5.6\text{ g}/\text{m}^2$ thick (one side) in a halide bath.

These tin-plated steel sheets were subjected to a reflowing operation by electric resistance heating and then subjected to a cathodic chemical treatment in sodium dichromate to provide two finished tin-plated steel sheets.

An ATC test, a hot water test and an iron solution test were carried out on each of the finished sheets, the results obtained being shown in Table 3.

TABLE 3

Kind of Samples	Test Results			
	ATC Value ($\mu\text{A}/\text{cm}^2$)	ISV ($\mu\text{g}/\text{cm}^2$)	Number of pinholes per 1 cm^2	Tin Crystal Size
Tin-plated steel sheet treated by the method according to the invention	0.024	0.05	0 to 10	# 8
Tin-plated steel sheet for comparison	0.190	0.31	30 to 50	# 8

Example 4.

A rimmed steel sheet was cold rolled, electrolytically cleaned in an alkaline liquid,

washed with water, slightly pickled, and then washed with water.

The rimmed steel sheet thus treated was

plated in a standard copper pyrophosphate plating bath with a copper coating of 0.10 μ thick. Several such copper plated steel sheets were washed with water, dried and then heated at 700°C for one minute, two minutes and five minutes respectively, so as to penetrate and diffuse the plating metal into the steel sheet to different extents.

These rimmed steel sheets plated with the copper coating and treated as above were

further electrolytically cleaned, washed with water, slightly pickled, again washed with water and then electroplated with a tin coating 5.6 g/m² thick (one side) in a halide bath.

These tin-plated steel sheets were subjected to a reflowing operation by electric resistance heating, and an ATC test was then effected thereon.

The results obtained are shown in Table 4.

TABLE 4

	Heating time		
	1 minute	2 minutes	5 minutes
ATC Value (μ A/cm ²)	0.120	0.045	0.055
Tin Crystal Size	# 12	# 9	# 9

It was recognised by electron diffraction that the plated copper layer remained on the steel sheet surface after it had been heated for 1 minute only and that this plating disappeared from the steel sheet surface to provide a reformed steel sheet surface after it had been heated for 2 minutes and 5 minutes respectively, the ATC values then becoming substantially a minimum.

Example 5.

A rimmed steel sheet was cold rolled, electrolytically cleaned in an alkaline liquid, washed with water, slightly pickled, and then washed with water.

The rimmed steel sheet thus treated was plated in a plating bath having the following composition, under the plating conditions indicated, with a nickel-tin alloy (Sn 65%) coating 0.10 μ thick.

Plating bath composition:

Nickel chloride (Hexahydrate) 250 g/l
Stannous chloride (Dihydrate) 50 g/l

Acidic ammonium fluoride 50 g/l
Plating condition:
pH 2.7
Bath temperature 65°C
Current density 2.7 A/dm²

Several such nickel-tin alloy plated steel sheets were washed with water, dried and then heated at 700°C for 1 minute, 2 minutes and 5 minutes respectively, so as to penetrate and diffuse the plating alloy into the steel sheet to different extents.

These steel sheets plated with the nickel-tin alloy coating and treated as above were further electrolytically cleaned, washed with water slightly pickled, again washed with water and then electroplated with a tin coating 5.6 g/m² thick (one side) in a halide bath.

These tin-plated steel sheets were subjected to a reflowing operation by electric resistance heating and an ATC test was then effected thereon.

The results obtained are shown in Table 5.

TABLE 5

	Heating time		
	1 minute	2 minutes	5 minutes
ATC Value ($\mu\text{A}/\text{cm}^2$)	0.160	0.050	0.070
Tin Crystal Size	# 12	# 9	# 9

It was recognised by electron diffraction that the plated nickel-tin alloy remained on the surface after the sheet had been heated for 1 minute only, and that this disappeared from the steel sheet surface to provide a reformed steel sheet surface when it had been heated for 2 minutes and 5 minutes, respectively.

WHAT WE CLAIM IS:—

1. A method of producing tin-plated steel sheet which comprises

(i) treating a steel sheet with nickel, copper or a nickel-tin alloy to form a coating thereon having a thickness of from 0.005μ to 0.5μ ;

(ii) heating the coated steel sheet in a non-oxidising atmosphere to completely diffuse the nickel, copper or nickel-tin alloy into the steel to form a reformed steel sheet; and

(iii) plating the reformed steel sheet with tin to form the desired tin-plated steel sheet.

2. A method according to claim 1 wherein the steel sheet is a rimmed steel sheet.

3. A method according to claim 1 wherein the steel sheet is a killed steel sheet.

4. A method according to any one of the preceding claims wherein the heating is carried out until the ATC value (as hereinbefore defined) of the sheet reaches a minimum.

5. A method according to any one of the preceding claims wherein heating is carried out at a temperature of from 600 to 800°C .

6. A method according to any one of the preceding claims wherein the heating is carried

out by a continuous annealing operation.

7. A method according to claim 6 when appendant to claim 5 wherein heating is carried out for a period of from 1 to 10 minutes.

8. A method according to any one of claims 1 to 5 wherein the heating is carried out by a box annealing operation.

9. A method according to claim 8 when appendant to claim 5 wherein the heating is carried out for a period of from 30 minutes to 10 hours.

10. A method according to any one of the preceding claims which comprises the additional step of reflowing the surface of the tin-plated steel sheet.

11. A method according to claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

12. A method according to claim 1 and substantially as hereinbefore described with reference to Figure 1, 2, 3A or 4B.

13. A tin-plated steel sheet whenever produced by a method according to any one of the preceding claims.

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Sheet 1

FIG. 1

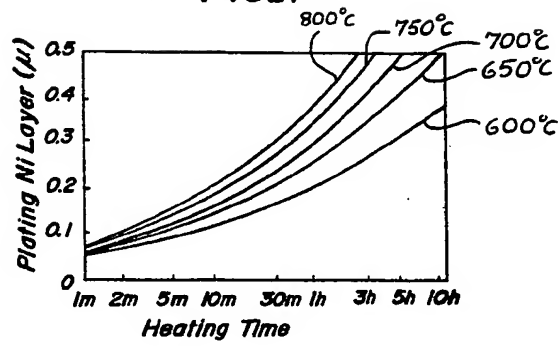
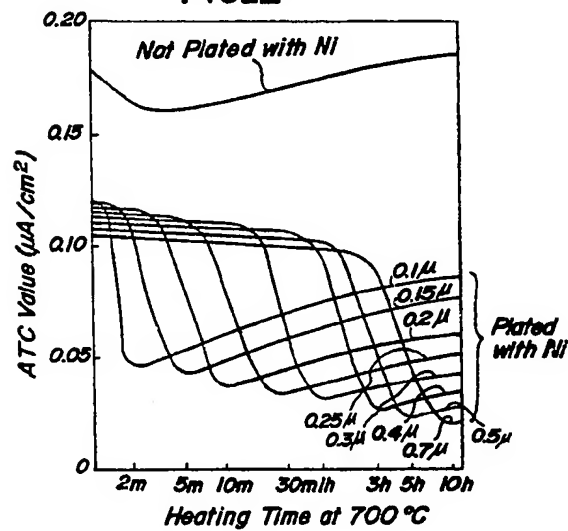


FIG. 2



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Sheet 2

FIG. 3A

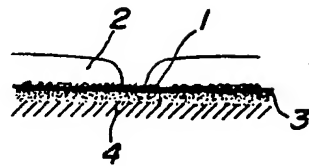


FIG. 3B

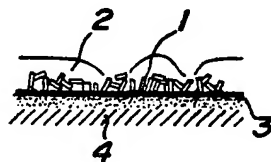
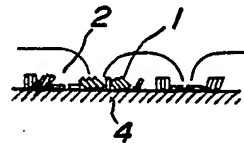


FIG. 3C



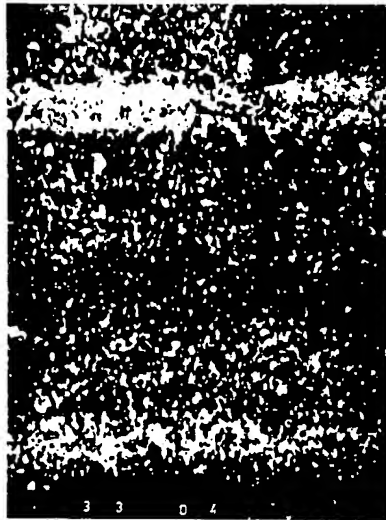
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FIG_4A



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FIG. 4B



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